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# **Enhancing Selective Catalytic Reduction of NO<sub>x</sub> with Alternative Reactants/Promoters**

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## **Abstract**

The hydrocarbon-selective catalytic reduction (HC-SCR) activity of an Ag/Al<sub>2</sub>O<sub>3</sub> catalyst was investigated. The function on catalytic NO<sub>x</sub> reduction of different fuel properties using alternative reactants such as gas-to-liquid (GTL) and butanol was studied. This work proves that such improvements are due to the high reactivity, polarity and diffusivity of butanol within the catalyst enhancing NO<sub>x</sub> conversion. Furthermore, it is suggested that HC components such butanol share some of the reaction mechanisms to hydrogen as a promoter in addition to his role as a reductant leading to improve NO<sub>x</sub> reduction. Therefore, it is proposed the simultaneous dual role of butanol as a reactant and as promoter.

Catalyst performance at low temperature was further improved with the addition of hydrogen (H<sub>2</sub>). However, this performance was found to degrade as temperature increases, due to H<sub>2</sub> reactant selectivity changing, directly being oxidised. Increased NO<sub>x</sub> conversion was dependent on HC:NO<sub>x</sub> ratio, showing at low temperature a low HC:NO<sub>x</sub> ratio is required. As temperature increases, so does the required HC:NO<sub>x</sub> ratio to compensate for hydrocarbons partial and complete oxidation. These results demonstrate a method of gaining significant NO<sub>x</sub> reduction through the combination of environmental catalysts and alternative reactants.

**Keywords:** HC-SCR, Alternative fuels, hydrogen, NO<sub>x</sub> conversion

## 1. Introduction

Diesel engines are becoming prominent due to the superior fuel efficiency over petrol engines [1]. However, the high levels of nitrous oxides (NO<sub>x</sub>), particulate matter and their trade-off limits their environmental benefits being required the use of after treatment to reduce pollutant emissions. NO<sub>x</sub> has become a significant pollutant within urban areas and is linked to health issues, acid rain and photo-chemical smog [2]. This has led to increasingly stringent legislation being implemented across Europe and the rest of the world to limit NO<sub>x</sub> emissions from all modes of vehicular transport. Diesel engines operate in lean-burn (excess of air) conditions meaning they cannot be treated by three way catalytic converters to reduce NO<sub>x</sub>, as in petrol engines [3]. Several key approaches have been identified (some already in commercial production) to reduce NO<sub>x</sub> emissions in diesel engines. The most used are lean NO<sub>x</sub> trap (LNT) [4][5], ammonia selective catalytic reduction (NH<sub>3</sub>-SCR) [6], their combination [6]-[7] and hydrocarbon-selective catalytic reduction (HC-SCR).

This research is focused on HC-SCR which could eliminate the need for a secondary fuel tank [8]-[12] and the use of expensive platinum group metal (pgm) loadings. A hydrocarbon (HC) containing reactant is injected into the exhaust gas upstream the HC-SCR catalyst and those hydrocarbons then react with the NO<sub>x</sub> on the catalyst's active sites to reduce the NO<sub>x</sub> levels downstream the catalysis. The fuel injected into the exhaust not only increases catalytic NO<sub>x</sub> conversion, but also helps to regenerate the catalyst via high temperature treatment with the fuel present preventing deactivation from sulphur poisoning/ageing [4]. The catalyst selected for this project is a silver aluminium oxide catalyst Ag/Al<sub>2</sub>O<sub>3</sub>, chosen as it is effective at NO<sub>x</sub> reduction over large temperature ranges with high thermal stability [3].

In previous studies it has been proven that the Ag/Al<sub>2</sub>O<sub>3</sub> performance is highly influenced by the hydrocarbon type injected into the system [13]-[17]. As paraffin HC chain length increases and becomes unsaturated, so does NO<sub>x</sub> conversion, allowing the catalyst to become more active and reducing NO<sub>x</sub> emissions at lower temperatures [3],[13],[18]. As chain length and unsaturation increases, coke production and rate of coke deposition on the catalyst increases, limiting NO<sub>x</sub>

reduction [3],[13],[15]. It has also been found that aromatic hydrocarbons increase coke deposition on the catalyst surface inhibiting the catalyst activity [3],[15]. Therefore, it has been previously showed that gas to-liquid (GTL) produced via the Fischer-Tropsch process which does not contain aromatic and unsaturated components has a higher de-NO<sub>x</sub> activity compared with conventional diesel [3].

Light alcohols specifically ethanol has been identified as good reductant, which assists in the performance of the Ag/Al<sub>2</sub>O<sub>3</sub> catalyst to selectively reduce NO<sub>x</sub> emissions [2][6],[14],[16]-[17],[19]. Chain lengths longer than butanol (C<sub>4</sub>) and shorter than ethanol (C<sub>2</sub>) were identified as significantly less reactive with the catalyst [14],[16]. There is still limited research using pure butanol [14],[16] and there is not research investigating the effect of butanol-diesel-like fuels over HC-SCR catalyst. Furthermore, the benefits of butanol when blended with diesel-like fuels in terms of blend fuel properties [20], combustion and emissions [21] has the potential to be used in the engine and as a reductant for the aftertreatment system.

From past studies hydrogen (H<sub>2</sub>) has been identified to significantly increase catalyst activity, (acting as a promoter) especially at low temperature when enough reductants are injected [16][18],[22]-[23]. This is thought to be caused by H<sub>2</sub> allowing the formation of reactive species at lower temperature and the oxidation of NO to NO<sub>2</sub> over the catalyst. This enables a larger NO<sub>x</sub> conversion to be gained at lower temperatures as well as a significantly reduction of coking on the catalyst surface [16],[23]. Based on the different mechanisms previously mentioned to explain the ‘hydrogen promoter effect’ on HC-SCR, similar mechanisms-effects are desirable to be found in the HC fuels.

The aim of this research is to investigate NO<sub>x</sub> abatement using HC-SCR to create a better understanding of the role that different types of hydrocarbons and hydrogen play in improving the catalytic activity of NO<sub>x</sub> reduction. It is believed that this knowledge will contribute in identifying HC components that promote the HC-SCR as the H<sub>2</sub> does. The investigation also considers whether the blending of the two reductants (butanol and GTL) keeps the good catalyst’s activity seen with light alcohols. Finally further tests have been conducted into how the catalyst performs at different

HC:NO<sub>x</sub> and H<sub>2</sub>:NO<sub>x</sub> ratios, to find enhanced performance conditions, at specific temperatures for the selected blend.

## 2. Materials and Methods

A schematic of the experimental installation used in this research is presented in Figure 1. The engine used was a single cylinder direct injection diesel engine producing the exhaust gas stream that was used for NO<sub>x</sub> reduction. The main engine specifications are detailed in Table 1. The engine was fixed with a running speed of 1500rpm and load set at 2bar indicated mean effective pressure (imep) whilst was operated by ultra low sulphur diesel (ULSD) fuel. Thermocouples (accuracy  $\pm 2.2^{\circ}\text{C}$ ) were placed in the system and connected to PicoLog software enabling real time temperatures to be continuously monitored at all times.

A low loading supported platinum based diesel oxidation catalyst (DOC) coated onto a cordierite honeycomb monolith substrate was placed in the exhaust system to eliminate the effect of any unburnt hydrocarbons from the combustion process which could influence the results (the DOC performance in reducing HC was around 60-70% for this engine operating condition). Thus, when measuring NO<sub>x</sub> reduction from HC injection it will only be caused by those that are injected into the exhaust system downstream the DOC. In the reactor, a SiC-Diesel Particulate Filter (DPF) was placed upstream the SCR to trap carbonaceous species, preventing them from blocking the active sites on the HC-SCR catalyst, alleviating the risk of poisoning. This was followed by the Ag/Al<sub>2</sub>O<sub>3</sub> 2% catalyst which was prepared by impregnating  $\gamma$ -alumina (surface area = 150m<sup>2</sup>/g) with aqueous AgNO<sub>3</sub> before drying and calcining in air for 2hours at 500°C to achieve a silver loading of 2wt%. This non-commercial catalyst provided by Johnson Matthey was made into an aqueous suspension, which was then uniformly coated onto ceramic monolith substrates ( $\varnothing = 115\text{mm}$ ,  $L = 75\text{mm}$ ) with a high cell density (600cpsi).

The NO<sub>x</sub> concentration was measured before and after every test in the different sampling points using a MultiGas 2030 Fourier Transform Infrared Spectroscopy (FTIR), to ensure stability of the testing and that the catalyst had not become deactivated. The engine exhaust emissions in the sampling points 2 and 3 as noted in Figure 1 (before and after hydrocarbons were injected,

respectively) were monitored and it was found that the NO<sub>x</sub> level stabilized at 300ppm. This enabled a constant HC:NO<sub>x</sub> ratio to be set. A constant Gas Hourly Space Velocity (GHSV) was set at 30kh<sup>-1</sup>. During testing concentrations of NO, NO<sub>2</sub>, N<sub>2</sub>O, CO, CO<sub>2</sub>, NH<sub>3</sub> and total un-burnt hydrocarbons were recorded using the FTIR analyser. Prior to perform the tests as well as at the end of each experiment, nitrogen was introduced to the FTIR inlet to avoid any contamination and or condensation of the residual hydrocarbons or water of the exhaust gases.

The injected reactants used in the study were GTL, ULSD, butanol and blends of GTL and butanol at 70%-30% and 30%-70% GTL-Butanol ratio (%v/v). The hydrocarbon components properties are listed in Table 2. From Table 2 it can be seen that the lubricity of the blends containing 30% and 70% (% v/v) of butanol as well as pure butanol are well above the recommended 460µm. However, the blend GTL70-Butanol30 is below the maximum value of 520µm allowable in a diesel engine. This means that the GTL70-Butanol30 blend could be used to operate the diesel engine and be used to enhance the de-NO<sub>x</sub> catalyst performance without the need of a secondary fuel tank.

The tests conducted are noted as follows:

- a) Influence of different type of reactants and their blends on HC-SCR NO<sub>x</sub> reduction performance. The different hydrocarbon components were injected individually into the exhaust system downstream of the DOC (as seen in Figure 1), through a heated line at 140°C. This used an electronic syringe pump to regulate the reactant flow rate and an atomiser, enabling the liquid fuel to be injected as a fuel mist, allowing better mixing with the exhaust gas. This ensured the reactant was injected at a set HC: NO<sub>x</sub> ratio of 3:1, chosen from previous tests [3],[24]. NO<sub>x</sub> conversion was then monitored on a continuous temperature ramp from 130-350°C. To confirm the reproducibility and significance level of the results, the tests were repeated three times for the pure components (e.g. GTL and butanol). Error bars have been calculated based on the standard deviation of the results considering a 95% confidence level.

- b) H<sub>2</sub> addition on NO<sub>x</sub> reduction. GTL, GTL70-Butanol30 and butanol were injected with and without H<sub>2</sub> (8000ppm) with a continuous temperature ramp from 130-350°C and an HC:NO<sub>x</sub> ratio of 3:1.
- c) Impact of HC:NO<sub>x</sub> (1:1, 3:1 and 6:1) and H<sub>2</sub>:NO<sub>x</sub> (8.34:1, 16.67:1 and 26.65:1) ratio on NO<sub>x</sub> reduction at different set temperatures. The selected temperatures included: i) a low temperature/activity region (180°C), ii) a reactive temperature region (230°C) and iii) high temperature region (330°C). The GTL70-Butanol30 blend was selected for this further testing due to its promising de-NO<sub>x</sub> selectivity and its superior lubricity properties compared to other blends.

### 3. Results and Discussion

#### 3.1 Influence of hydrocarbon components on NO<sub>x</sub> reduction performance

Figure 2 shows that the Ag/Al<sub>2</sub>O<sub>3</sub> catalyst without HC injection has poor de-NO<sub>x</sub> performance being lower than 10% (passive conditions). Conventional diesel fuel was injected to provide a base level that can be gained from diesel-like fuels (50%). When GTL was injected, a continuous superior NO<sub>x</sub> conversion was obtained compared to ULSD over the entire temperature range. This is due to aromatic and unsaturated hydrocarbon content of ULSD which are prolific in causing catalyst coking (<250°C) [6],[14],[24] as well as the longer paraffin chain length of GTL which has been reported to be more reactive for de-NO<sub>x</sub> catalytic activity in Ag/Al<sub>2</sub>O<sub>3</sub> catalysts [3]. On the other hand, the effect of butanol depends on the temperature as it is explained as follows.

##### *a) Low-medium temperature*

The increased Ag/Al<sub>2</sub>O<sub>3</sub> activity at low-medium temperature demonstrated a strong dependence on the butanol level contained within the mixture. Figure 2 shows that the increasing butanol level promotes the catalyst activity at low temperature and demonstrates that with butanol higher levels of performance are achieved compared with GTL. The combination of several factors is proposed here to explain the dual role of butanol as a reactant and promoter resulting in superior catalytic activity at those temperatures:

i) Reactivity. It is suggested that at low temperature butanol has high activity to react with active oxygen components (e.g. superoxide  $O_2^-$ ). Active intermediates such as butyraldehyde is produced, which is very reactive [6],[14] to produce ammonia to react with  $NO_x$  to produce nitrogen, water and CO<sub>x</sub> species. The high reactivity of butanol and its intermediates at low temperature is confirmed by the higher consumption of THC and NO reduction compared to GTL (see Figure 3).

ii) Production of active oxygenated components. It is proposed the possibility that oxygenate hydrocarbon components such as butanol could enhance the formation of active oxygenated components to produce  $NO_2$  and  $O_2^-$  (superoxide) [22],[25] enhancing catalyst's performance. The higher production of  $NO_2$  at low temperatures in the case of butanol and its blend can be confirmed in Figure 3. At very low temperature (lower than 160°C)  $NO_2$  emissions downstream the catalyst are negligible for all the reactants. However, it is suggested that in the case of butanol the NO to  $NO_2$  reaction is in excess enhanced at low temperature, hence some of the  $NO_2$  formed within the catalyst (between 170-200°C) is not reduced to nitrogen. In the case of GTL the excess of  $NO_2$  production occurs at higher temperatures (200-270°C) compare to butanol. In the case of the GTL-Butanol blend two small  $NO_2$  peaks are observed, the first one at low temperature corresponding to butanol and the other one at higher temperature corresponding to GTL.

iii)  $NH_3$  production. Butanol and its intermediates are more reactive than GTL producing a higher production of  $NH_3$  within the catalyst. This higher production of ammonia within the catalyst can also contribute to the high reduction of  $NO_x$  emissions with butanol via  $NO-NH_3$ ,  $NO_2-NH_3$  and  $(NO+NO_2)-NH_3$  (fast-SCR) reactions. Nevertheless, once  $NO_2$  is totally consumed,  $NH_3$  cannot be used within the catalysis resulting is some  $NH_3$  slippage when pure butanol is used.

iv) Polarity. Alcohols are polar and water soluble in nature which enable them to compete successfully with water for adsorption sites on the catalyst [14].

v) Diffusivity and chain length. The low molecular mass, low viscosity and short chain length of butanol are factors which provide a higher diffusivity compared to most of the hydrocarbon components present in GTL. This would result in an easier accessibility to the catalyst active sites



where the surface reactions occur to reduce NO<sub>x</sub> emissions. Furthermore, longer chain length components could create olefins by the dehydration reaction which will easily polymerize yielding coke deactivating the catalysts. Coke formation due to olefin polymerization will be higher with the increase of the chain length.

*b) High temperature*

On the other hand, there is considerable fall-off shown at high temperatures for all reactants achieving almost the same performance at temperatures above 330°C. The reason for this is that as temperature increases, so does the required HC:NO<sub>x</sub> ratio, to compensate for hydrocarbons direct oxidation with O<sub>2</sub>. This direct oxidation begins to be dominant at these higher temperatures as reductant selectivity changes [16]. This means hydrocarbons injected are less likely to be broken down into usable NO<sub>x</sub> reducing species over the Ag/Al<sub>2</sub>O<sub>3</sub> catalyst. It can also be observed from Figure 2 that as the butanol level increases, so does the NO<sub>x</sub> conversion drop off at higher temperatures. This may suggest that the reductant selectivity of butanol changes at a faster rate compared with GTL and ULSD at these high temperatures.

The formation of nitrous oxide (N<sub>2</sub>O) which is known to be a harmful greenhouse gas promoter has been also studied. It is known that NO<sub>x</sub> can be reduced to N<sub>2</sub>O in the presence of hydrocarbon species under low exhaust gas temperatures over platinum catalyst. However, it has to be noted that in this case where a Ag/Al<sub>2</sub>O<sub>3</sub> catalyst is used the N<sub>2</sub>O emissions are low (lower than 15ppm) for all the reductants (see Figure 3).

Due to the varying chain length, density and molecular mass of the different blends used in these experiments, the fuel flow rates were different for every reactant injected to obtain the same HC:NO<sub>x</sub> ratio. Therefore, a higher fuel flow rate is required for butanol and its blends compared to GTL, due to the shorter carbon chain length of butanol. However, fuel penalty can be calculated as the proportion of the energy of the reductant injected to obtain the desired HC:NO<sub>x</sub> compared to the fuel energy required to operate the engine (see Table 3). It can be observed that as the butanol level increases, the

penalty caused from the HC injection is maintained constant or even falls slightly. Therefore, the incorporation of butanol results in higher de-NO<sub>x</sub> activity for similar energy penalty compare to GTL.

### 3.2 Impact of H<sub>2</sub> addition on NO<sub>x</sub> reduction performance with different reactants

In Figure 4 it can be seen that the addition of H<sub>2</sub> allows the fuels to be more active at lower temperatures, shifting the peak temperatures of GTL and GTL70-Butanol30 to 230°C and butanol from 240°C to 200°C. This shows that in the presence of hydrogen, butanol still is able to act as a promoter enhancing NO<sub>x</sub> conversion at low temperature, with GTL70-Butanol30 consistently outperforming GTL at temperatures up to 220°C. The addition of hydrogen to the GTL70-Butanol30 resulted in a similar performance to that of butanol without H<sub>2</sub> injection. As in the previous section, the hydrogen effect is explained also depending on the exhaust temperature.

#### *a) Low-medium temperature*

i) Activation of O<sub>2</sub>. Based on the obtained results, it is suggested that hydrogen promotes the activation of molecular O<sub>2</sub> into reactive species (e.g. O<sub>2</sub><sup>-</sup>) which enhances NO<sub>x</sub> reduction within the catalyst in the different steps of the HC-SCR mechanism as it is explained below.

- 1) HC conversion. Comparing between Figure 3 and Figure 5, it can clearly be seen that for all fuels the presence of H<sub>2</sub> significantly increases the total HC conversion. It is suggested that these oxygen species are reactive towards the C-H bonds of the injected hydrocarbons [22],[26] which enable the formation of active hydrocarbon components from the parent reactant to reduce NO<sub>x</sub>.
- 2) Ammonia production. These active oxygen species also can take part in the production of ammonia as well as in the activation of NH<sub>3</sub> to reduce NO and NO<sub>2</sub> to N<sub>2</sub> [25]. Figure 5 shows that ammonia slippage is produced at lower temperature when butanol and hydrogen are combined with respect to the rest of studied conditions (Figure 3). Therefore, it is thought that NH<sub>3</sub> production is enhanced at low temperature by both hydrogen addition and butanol, further reacting with NO and NO<sub>2</sub> to produce N<sub>2</sub>. However, once NO<sub>2</sub> is fully reduced there is

ammonia slippage as it cannot find enough  $\text{NO}_2$  to react with as well as being limited the fast-SCR reaction. In the case of butanol the consumption of  $\text{NO}_2$  and appearance of  $\text{NH}_3$  slippage occur at lower temperature compare to GTL. However, in the GTL-Butanol blend  $\text{NH}_3$  slippage is minimal; it is though that the enhancement in the ammonia production is optimal for the  $\text{NO}/\text{NO}_2$  availability, limiting ammonia slippage to a very low concentration (lower than 15ppm) for all the studied temperature range.

3)  $\text{NO}_2$  production. Furthermore, these species also enhance the  $\text{NO}$  to  $\text{NO}_2$  conversion, enabling  $\text{NO}_2$  to be more readily converted to the desired  $\text{N}_2$  [22],[25]. With the addition of hydrogen the  $\text{NO}_2$  peak is produced at lower temperature than without hydrogen for all the studied reactants (see Figure 3 and Figure 5). It has to be noted the high reactivity of butanol which enables the produced  $\text{NO}_2$  to be consumed within the catalyst at lower temperatures than in the case of GTL. It is suggested that this  $\text{NO}_2$  can be reduced with the  $\text{NH}_3$  created in the intermediate steps producing the desired  $\text{N}_2$ .

ii) Removal of nitrates. The addition of  $\text{H}_2$  also enables the removal of strongly adsorbed nitrates from the catalyst's active sites and support which, previously at low temperatures would have inhibited  $\text{NO}_x$  conversion [27]-[28].

iii) Removal of carbon deposits. Hydrogen promotes the oxidation of  $\text{NO}$  to  $\text{NO}_2$  which could oxidise the carbon deposits at low temperature, removing the carbon-rich surface species which inhibit the SCR reaction [15].

iv) Improve the selectivity to  $\text{N}_2$ . According to [29] the addition of hydrogen increases the selectivity to  $\text{N}_2$  in the de- $\text{NO}_x$  reaction by lowering the amount of hydrogen cyanide ( $\text{HCN}$ ) downstream the catalyst.

#### *b) High temperature*

At temperatures above  $300^\circ\text{C}$ ,  $\text{H}_2$  addition becomes less effective in the de- $\text{NO}_x$  reactions with all reactants. It is suggested that there is a change in the hydrocarbon selectivity and hydrogen enhances

hydrocarbon oxidation to CO<sub>x</sub> rather than promoting the HC-SCR reactions, producing a shortage of the reductant available for NO<sub>x</sub> removal. Furthermore, H<sub>2</sub> can be also consumed by O<sub>2</sub> rather than the reductant [16] directly forming H<sub>2</sub>O and heat, neither advantageous for de-NO<sub>x</sub> performance.

The effect of H<sub>2</sub> on the N<sub>2</sub>O formation can be observed in Figure 5. When hydrogen was added it slightly enhanced N<sub>2</sub>O formation at low temperature. It is suggested that at these low temperatures N<sub>2</sub>O can be formed by both H<sub>2</sub>-SCR and through the conventional HC-SCR reaction. N<sub>2</sub>O production is higher and at lower temperature for butanol as it has been shown to be the most reactive hydrocarbon. At temperatures above 250°C, no N<sub>2</sub>O is formed within the catalyst for any of the conditions studied.

### **3.3 Impact of HC:NO<sub>x</sub> and H<sub>2</sub>:NO<sub>x</sub> ratio**

In Figure 6 can be seen that at low temperature (180°C) the butanol within the blend (GTL70-Butanol30) has a positive effect in NO<sub>x</sub> conversion. However, larger additions of this blend decreased the catalyst performance, even though the higher availability of butanol (as a constituent of the blend). This decrease in performance of the Ag/Al<sub>2</sub>O<sub>3</sub> catalyst can be attributed to the excessive concentration of other reductants (e.g. HC components present in the GTL) not being able to break down at this low temperature into usable species over the catalyst blocking the active sites on the catalyst.

Clear stepped improvements are seen with the addition of H<sub>2</sub>, implying that it allows the catalyst to increase activity at low temperatures. It is shown that the optimal HC:NO<sub>x</sub> ratio at the low temperature is approximately 1:1 gaining maximum efficiency with the addition of H<sub>2</sub>. The Ag/Al<sub>2</sub>O<sub>3</sub> catalyst performance in reducing NO<sub>x</sub> at 220°C can be seen in Figure 7. The addition of H<sub>2</sub> for all conditions allows the catalyst to be more effective with conversion level up to 95%. There is a slight reduction in performance of the catalyst with increasing fuel injection from 3:1 HC:NO<sub>x</sub> ratio to 6:1, highlighting that adding extra fuel would be inefficient. This result demonstrates that a higher HC:NO<sub>x</sub> ratio is required at this higher temperature to gain the maximum NO<sub>x</sub> conversion. At the highest studied temperatures, the hydrocarbon level needed into the system increases to obtain high NO<sub>x</sub> conversion. On the other hand, the addition of H<sub>2</sub> is ineffective on the NO<sub>x</sub> conversion, with

limited or no benefit for all conditions tested. The optimal HC:NO<sub>x</sub> ratio was found to be at 6:1 without H<sub>2</sub> addition. This different behaviour of hydrogen depending on the temperature and hydrogen level suggest that hydrogen is not a reactant/reducing agent over the Ag/Al<sub>2</sub>O<sub>3</sub>, but a promoter of the de-NO<sub>x</sub> activity over Ag/Al<sub>2</sub>O<sub>3</sub> catalysts at low temperature [30] supported by the mechanisms previously explained.

From Table 4 it is clear that as the required HC:NO<sub>x</sub> ratio increases with temperature, there will be an increasing fuel penalty required to maintain a significant level of NO<sub>x</sub> reduction. This is caused by the need to inject a considerably larger proportion of the fuel upstream of the Ag/Al<sub>2</sub>O<sub>3</sub> catalyst to obtain the required HC:NO<sub>x</sub> ratio, making it less attractive in high temperature regions. Overall the results show that at higher temperatures (above 300°C), H<sub>2</sub> consistently loses its benefit as promoter, which supports past research papers on H<sub>2</sub> addition into HC-SCR catalysts [16],[22],[25],[28]. In addition Figures 6, 7 and 8 also demonstrate that as temperature increases the optimal HC:NO<sub>x</sub> ratio also increases, which is consistent with expectations.

#### **4. Conclusion**

This research has investigated an approach to control NO<sub>x</sub> emissions from a diesel engine using alternative reactants and hydrogen in HC-SCR technology. By studying the trends in NO<sub>x</sub> conversion, it can be seen that increasing the level of butanol promotes the Ag/Al<sub>2</sub>O<sub>3</sub> catalyst to attain higher activity in reducing NO<sub>x</sub> especially at low temperature. It is suggested the dual role of butanol as a reductant and as promoter sharing some of the hydrogen mechanisms favouring the production of NO<sub>2</sub> and NH<sub>3</sub> within the catalyst enhancing NO<sub>x</sub> conversion. The addition of H<sub>2</sub> as a promoter to the system also allows the catalyst to become more active at lower temperatures. It is thought that hydrogen promotes the activation of molecular oxygen on the catalysis surface to reactive oxygen resulting in higher production of active hydrocarbon species, NO<sub>2</sub> and NH<sub>3</sub> within the catalysis enhancing the de-NO<sub>x</sub> mechanism. Therefore, hydrogen combined with the incorporation of butanol to diesel-like fuels will allow the catalyst to be more active over a larger period in a wide temperature range (130-350°C).

Overall several findings from this research can be recommended for the combination of Ag/Al<sub>2</sub>O<sub>3</sub> catalyst and alternative hydrocarbons to reduce NO<sub>x</sub> emissions. HC:NO<sub>x</sub> ratios affect NO<sub>x</sub> conversion and the ratio required for high NO<sub>x</sub> reduction increase with temperature to compensate for reductant selectivity changing. The addition of H<sub>2</sub> is effective at low-medium temperature while at temperature above 300°C, H<sub>2</sub> is no longer effective being more effective increasing HC injection to enhance the catalyst's performance. Therefore, the fuel penalty can be minimised by injecting the correct level of hydrocarbons and hydrogen into exhaust systems to take into account changing temperatures. Further investigation is needed to assess the feasibility of different methods to transport or to on-board produce hydrogen. An approach could be exhaust gas reforming converting hydrocarbon components as the proposed here to hydrogen rich gas.

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## Tables

**Table 1:** Engine specifications

Engine Specification	Data
Number of cylinders	1
Bore/Stroke	98.4mm/101.6mm
Connecting Rod Length	165mm
Displacement Volume	733cm <sup>3</sup>
Compression Ratio	15.6:1
Rated Power	8.36Kw@2500rpm
Peak Torque	39.2Nm@1500rpm
Injection System	Three holes pump-line-nozzle
Injection Timing	22°bTDC
Engine Piston	Bowl-in-piston

**Table 2:** Fuel properties

Fuel Property	GTL	ULSD	Butanol	GTL70-Butanol30	GTL30-Butanol70
Chemical Formula	C <sub>18.4</sub> H <sub>38.8</sub>	C <sub>14</sub> H <sub>26.09</sub>	C <sub>4</sub> H <sub>10</sub> O	C <sub>9.64</sub> H <sub>21.27</sub> O <sub>0.61</sub>	C <sub>5.52</sub> H <sub>13.05</sub> O <sub>0.89</sub>
Density (kg/m <sup>3</sup> )	784.60	827.10	809.50	792.07	802.03
Viscosity (cSt)	3.5	2.7	2.22	2.38	2.26
Heating Value (MJ/kg)	43.90	2.47	33.12	40.16	35.27
Wear Scar 1.4 (μm)	395	312	620	513	590
Aromatics (wt%)	0	43.30	0	0	0

**Table 3:** Fuel penalty constant HC:NO<sub>x</sub> ratio

Fuel	Fuel Penalty
GTL	5.09%
Diesel (ULSD)	5.29%
GTL70-Butanol30	5.03%
GTL30-Butanol70	4.97%
Butanol	4.90%

**Table 4:** Fuel penalty variable HC:NO<sub>x</sub> ratio

HC:NO <sub>x</sub> Ratio	Fuel	Fuel Penalty
1:1	GTL70-Butanol30	3.36%
3:1	GTL70-Butanol30	5.03%
6:1	GTL70-Butanol30	8.95%

## **Figure Captions**

**Figure 1:** Schematic of experimental facility

**Figure 2:** Reactant effect on NO<sub>x</sub> conversion over Ag/Al<sub>2</sub>O<sub>3</sub> catalyst at HC:NO<sub>x</sub>=3:1

**Figure 3:** Reactant effect on THC, CO, NO, NO<sub>2</sub>, N<sub>2</sub>O and NH<sub>3</sub> concentration downstream the HC-SCR catalyst

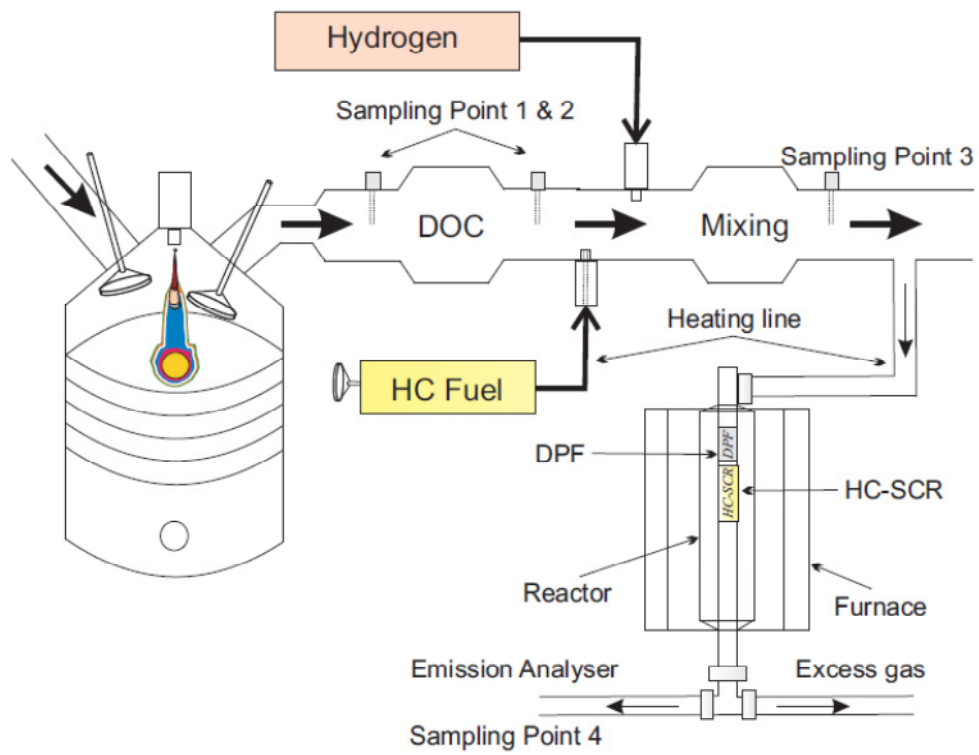
**Figure 4:** Impact of H<sub>2</sub> addition on NO<sub>x</sub> reduction over Ag/Al<sub>2</sub>O<sub>3</sub> catalyst with HC:NO<sub>x</sub>=3

**Figure 5:** Hydrogen and reactant effect on THC, CO, NO, NO<sub>2</sub>, N<sub>2</sub>O and NH<sub>3</sub> concentration downstream the HC-SCR catalyst

**Figure 6:** GTL70-Butanol30 impact on NO<sub>x</sub> reduction over Ag/Al<sub>2</sub>O<sub>3</sub> catalyst at 180°C exhaust temperature

**Figure 7:** GTL70-Butanol30 impact on NO<sub>x</sub> reduction over Ag/Al<sub>2</sub>O<sub>3</sub> catalyst at 230°C exhaust temperature

**Figure 8:** GTL70-Butanol30 impact on NO<sub>x</sub> reduction over Ag/Al<sub>2</sub>O<sub>3</sub> catalyst at 330°C exhaust temperature



**Figure 1**

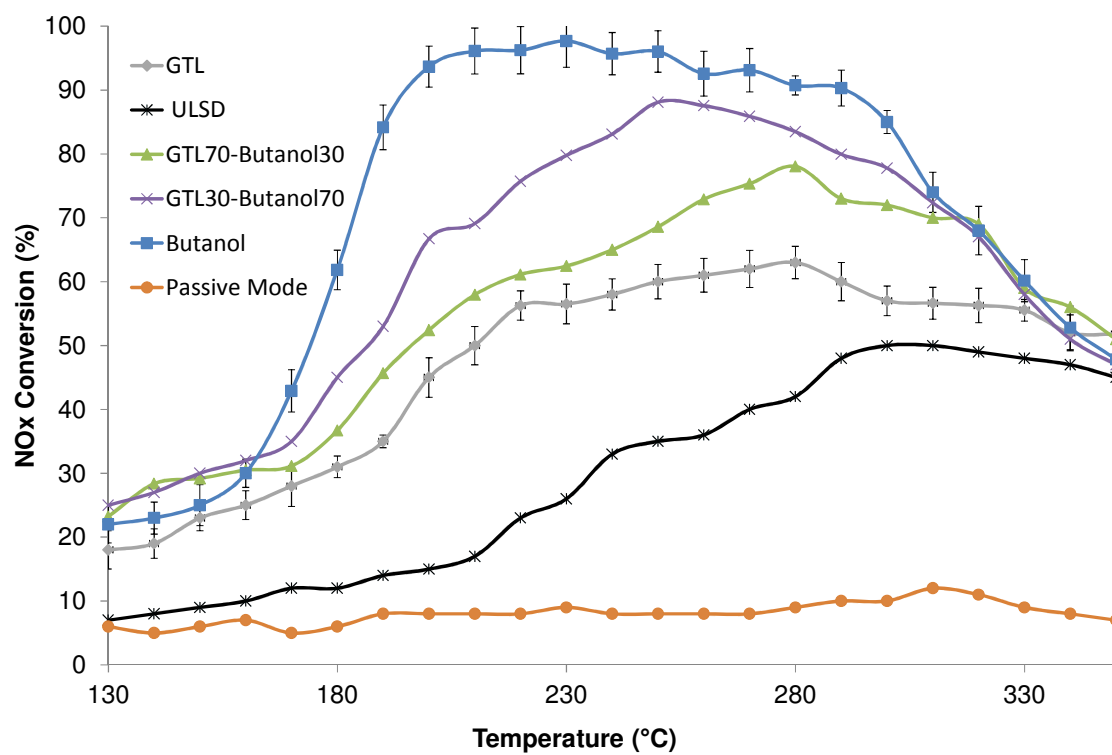
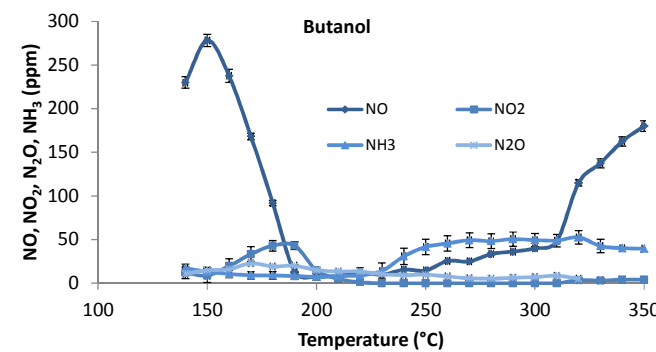
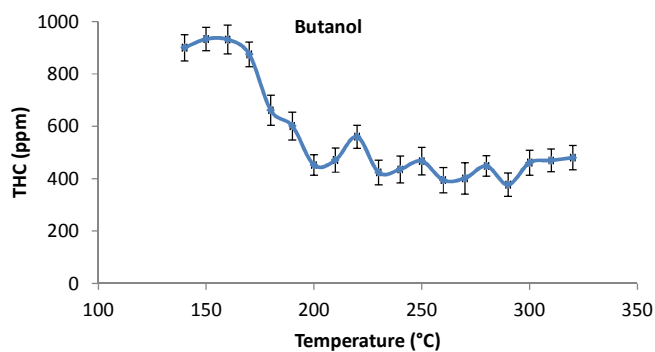
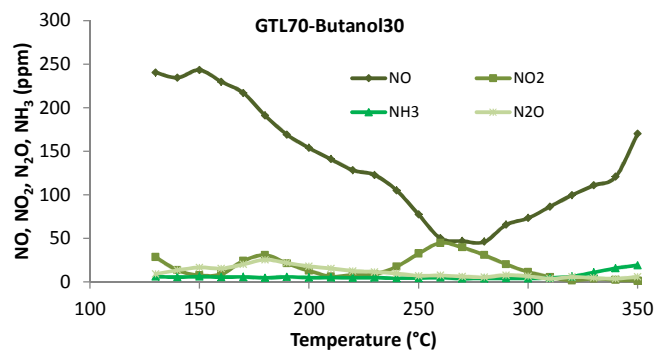
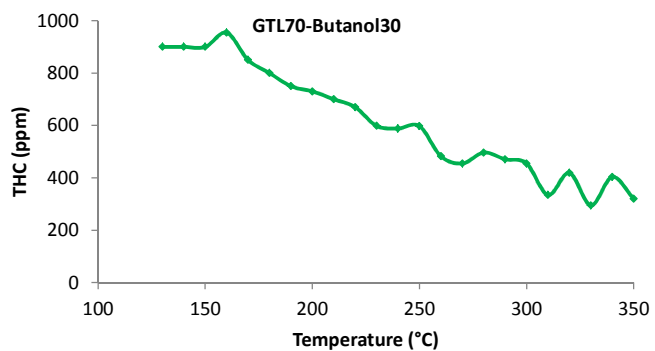
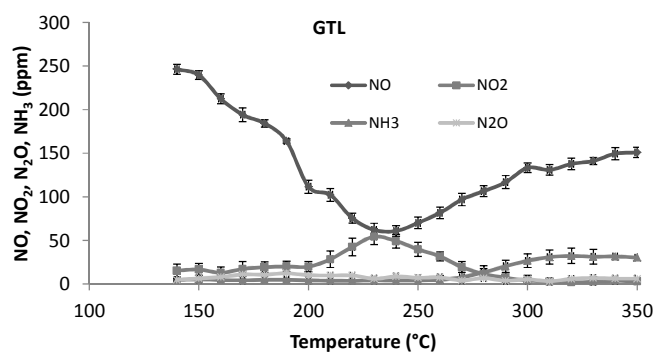
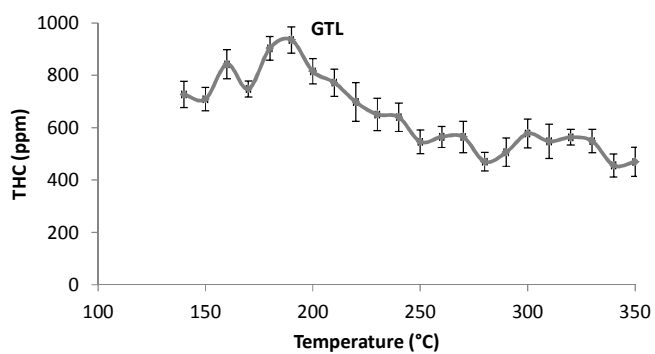


Figure 2



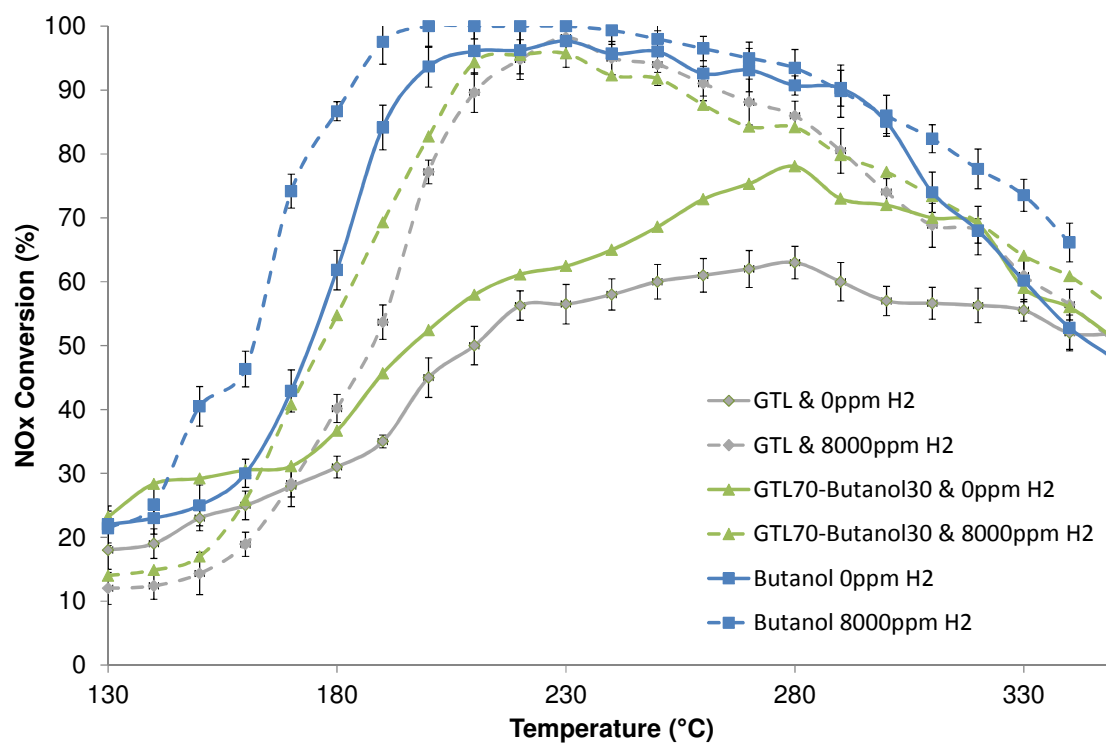
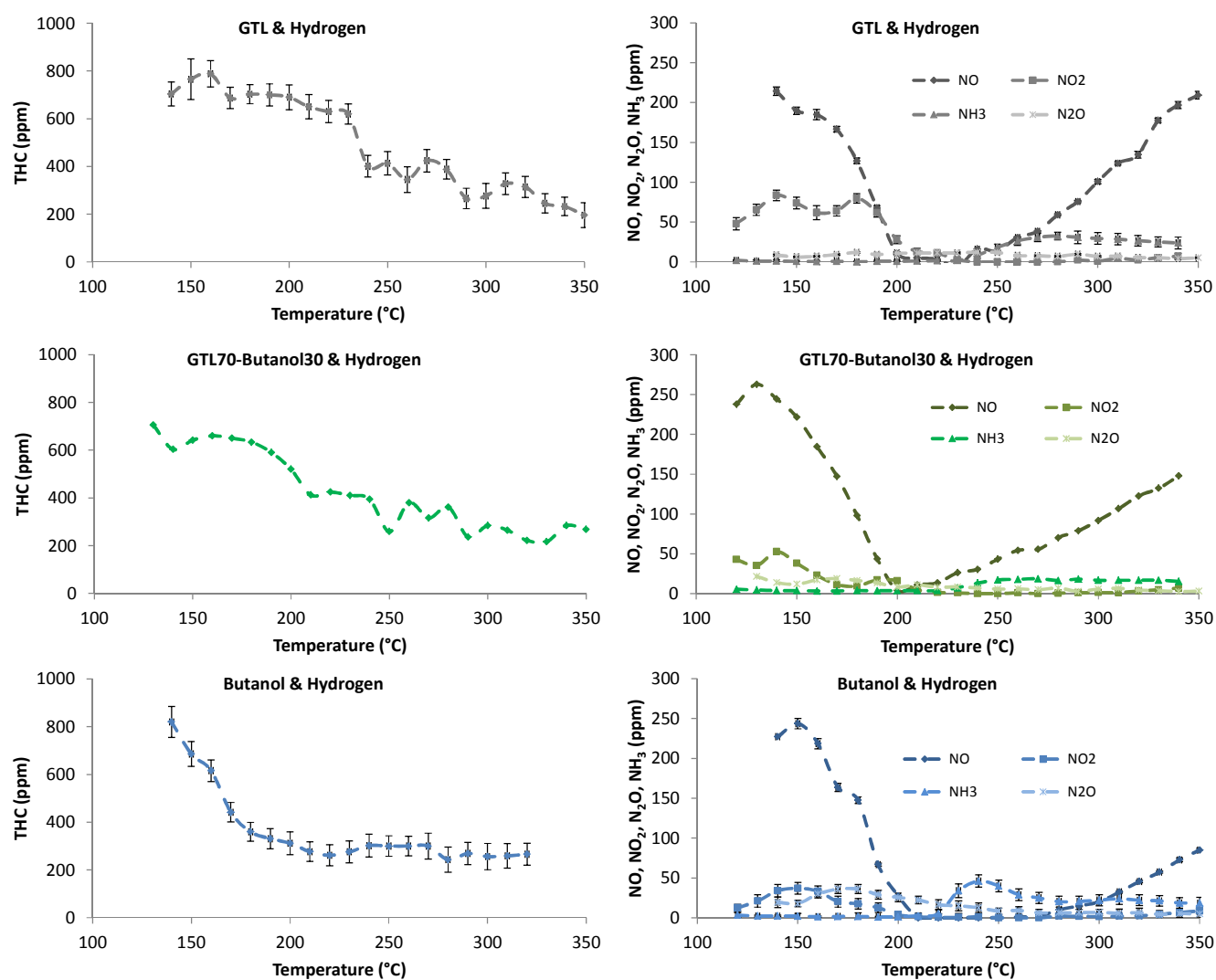
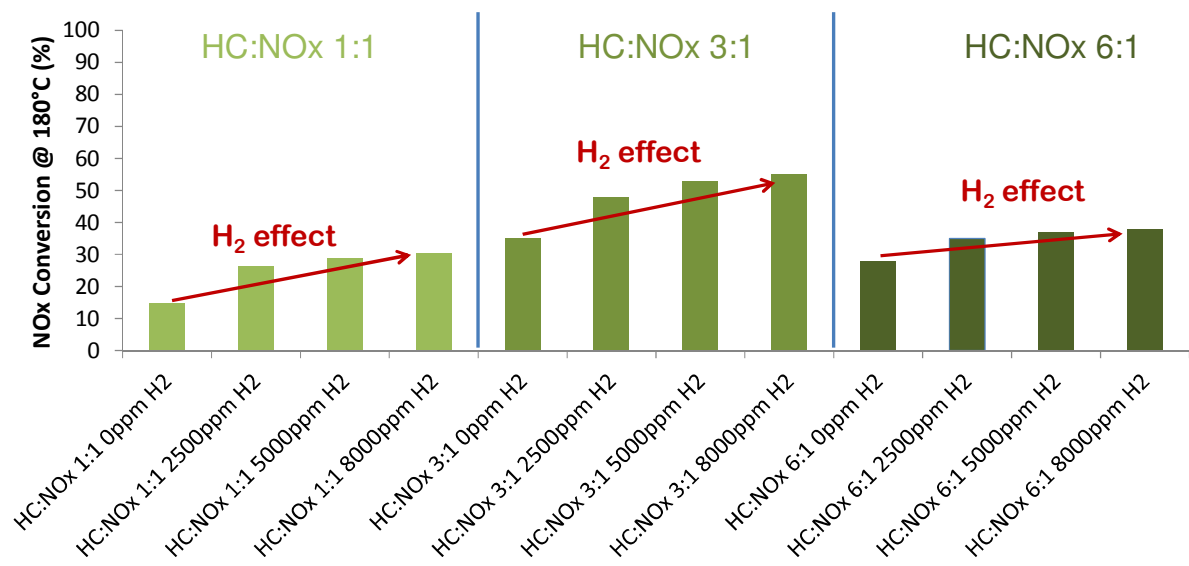


Figure 4

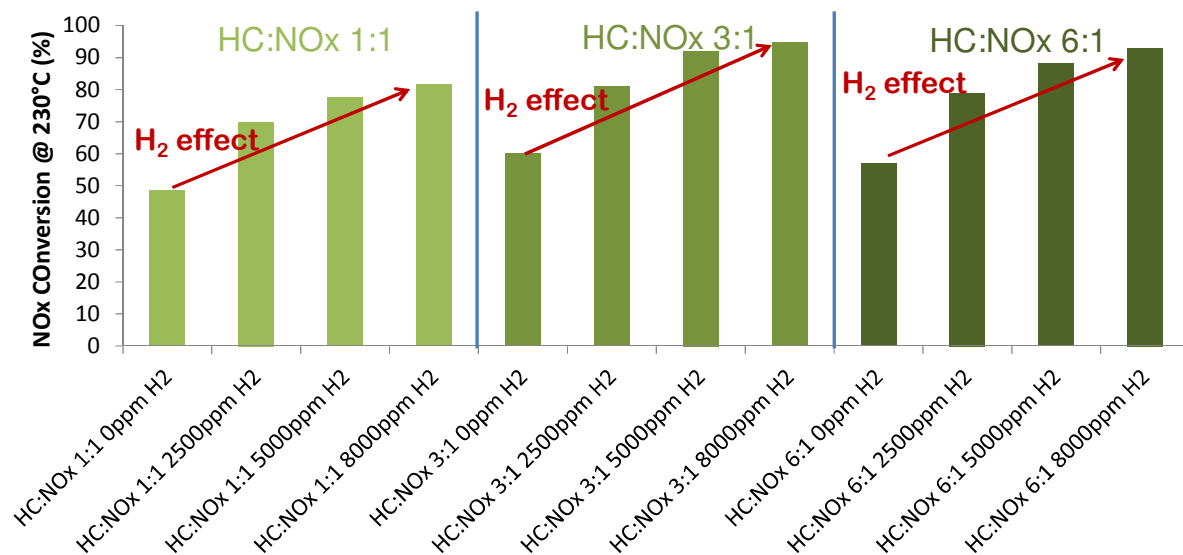


**Figure 5**

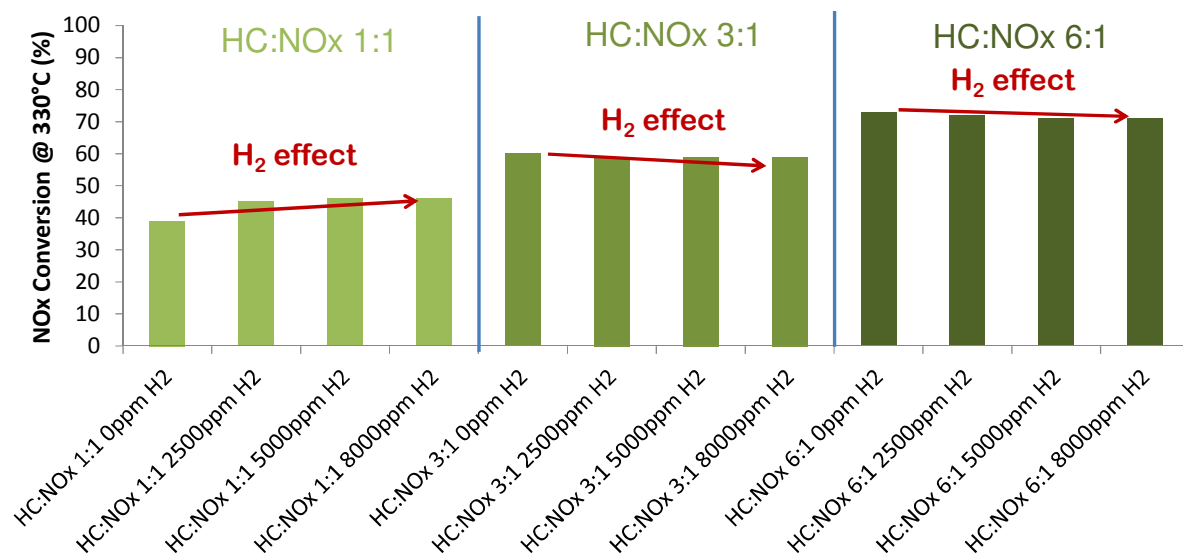




**Figure 6**



**Figure 7**



**Figure 8**